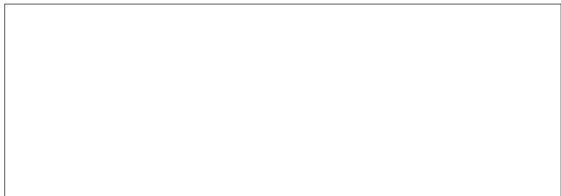


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(Technical Proposal



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(PHOTO GALVANIC CELL RESEARCH)

Prepared January 28, 1959

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Technical Proposal

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P H O T O G A L V A N I C C E L L R E S E A R C H

I. I N T R O D U C T I O N

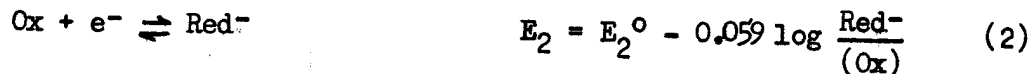
A program is proposed for the study and development of electrolytic batteries which operate normally (without irradiation) but which can be recharged by either optical or nuclear radiation. Particular emphasis is to be placed on the utilization of solar energy as a means of recharging the battery.

The photolysis of silver halides has been studied extensively in connection with the development of photographic processes;¹ and batteries in which silver is consumed to form a silver halide during discharge have been developed recently in several laboratories, especially for high temperature applications.² However, no research has been done, to our knowledge, on the effect of light on batteries of this type or on any other batteries comprising a light-sensitive discharge product. Yet, such research could open an alternate approach, both to the utilization of radiant energy and to the development of batteries with very long lifetimes and very high energy-to-weight ratios.

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- 1 C.E.K. Mees "Theory of the Photographic Process" (Macmillan Co., New York, 1946), and references quoted therein.
 - 2 J.L. Weininger "Iodine Activated Solid Electrolyte Cell for Use at High Temperature," General Electric Res. Laboratory, Report No. 58-RL-1957, May, 1958.

II. TECHNICAL DISCUSSION

Given a battery deriving its electromotive force E from the difference between the potential E_1 and the potential E_2 of the following half-cell reactions:



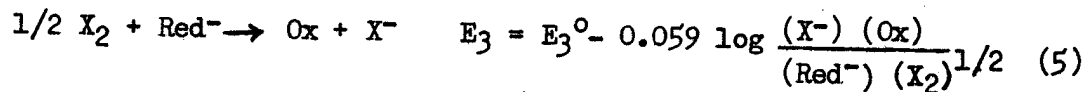
so that the over-all reaction on discharge is



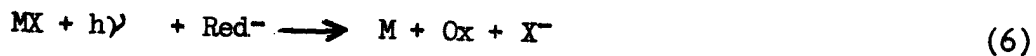
where MX is a light sensitive, rather insoluble salt of a metal M (silver or mercury) and a halogen X (I, Br, Cl or F), Red^- and Ox are components of a suitable oxidation-reduction couple, and (X^-) , (Red^-) , (Ox) are the concentrations of the respective species in the aqueous electrolyte. Upon suitable irradiation of the light-sensitive discharge product MX , photolysis occurs:



which will be accelerated if the halogen product is removed through the secondary reaction:

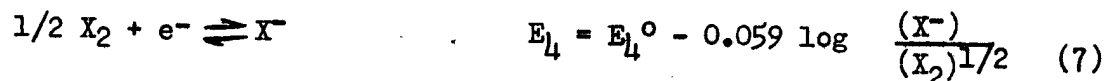


so that the over-all resulting reaction, (4) + (5), is



which is the reverse of reaction (3); i.e., the battery is effectively recharged by light.

Reaction (5) can occur only if the potential E_3 is positive, which is tantamount to the condition that the potential E_4 for the reaction:



be higher than E_2 . Furthermore, since reaction (3) must also give us a positive potential, it follows that

$$E_1 < E_2 < E_4. \quad (8)$$

This imposes one limitation on the choice of a suitable oxidation-reduction couple.

According to the generally accepted Mott-Gurney theory,³ photolysis of silver halides occurs through the excitation of an electron into a higher energy state or "conduction band":



followed by trapping of the freed electron at a so-called "speck" or trapping center T:



followed by diffusion of an Ag^+ ion to the negatively charged trap T^- with resulting emptying of the trap and formation of metallic silver:



Obviously, reaction (4) is the net result of reactions (9) through (11).

If high-energy nuclear particles are substituted for optical radiation, then reactions similar to (9) occur, the main distinction being that a single nuclear particle excites a large number of electrons into the conduction level in a very narrow region and in a very short time (less than 10^{-13} sec.). Although this would be expected to result in inefficiency through recombination of the closely spaced ion pairs:



experimental evidence³ on low velocity α -particles (< 10 Mev) suggests that more than one silver atom could be recovered from AgCl per 30 ev of energy, so that an α -particle from polonium (5.3 Mev) would produce at least 180,000 Ag atoms. If the battery e.m.f. (E) is about 0.6 v. (as in our Ag, FeCl_3 , Pt cells), then the fraction of radioactive energy utilized by the recharging process would be about 0.6 ev/30 ev or 2%. This estimated efficiency may be too conservative, however, because at higher temperatures (which must result from the appreciable energy dissipation) the efficiency of the photolytic process increases markedly.

3. J. H. Webb, Physical Review 74, Pages 511-532 (1948).

The undesirable recombination reaction (12) may also give rise to inefficient conversion of optical radiation into electricity under conditions of intense illumination (e.g., solar radiation in outer space or even on the earth's surface) and saturation of the traps T (i.e., low initial trap concentrations and slow rate of emptying of traps at low temperatures). Another undesirable parasitic reaction might be the attack of Ag by the photolytically formed halogen:



and the direct attack of Ag by Ox ; i.e., occurrence of reaction (3) in a single step without the accompanying production of electrical work. The purely physical problems must also be considered: internal resistance of the cell, overvoltage under heavy loads, and, what is most important, limited spectral response of the MX salt and filtering out of useful radiations by the electrolyte, the container walls and the photolytically formed silver.

Ideally, if the above parasitic reactions and interfering factors were absent, the quantum yield of the recharging reactions (4), (6), and (9) would be 100%, i.e., each photon of light absorbed would recover one silver atom. It becomes possible then to set an upper efficiency limit by considering that:

- (a) The silver halides absorb most photons with energies of 3 ev or more (i.e., with wavelengths of about 5000Å or less), which amounts to about 25% of solar radiant energy.
- (b) In solar radiation, the average photon energy for all photons of 3 ev or higher is about 3.7 ev.
- (c) The value of E must be less than 1.0 v, according to condition (8) and tables of standard oxidation potentials.⁴

This upper limit then becomes $25\% \times \frac{1.0\text{ev}}{3.7\text{ev}}$ or approximately 7%.

On the other hand, if it proved practical to extend the absorption spectrum of the halide down to about 1 ev by the addition of a minute quantity of suitable sensitizing or "hypersensitizing" dyes such as those used in color or infrared photography (or even simply by the formation of colloidal silver in the silver halide), then this upper limit could be raised to about 40%. Thus, a minor change in the make-up of the battery could increase its potential efficiency almost six-fold.

⁴ W. Latimer and J. H. Hildebrand, "Reference Book of Inorganic Chemistry" (Macmillan Co., New York, 1950) pp. 474-478.

However, our experimental studies have been thus far confined mainly to pure AgCl electrodes immersed in solutions of FeCl_3 and FeCl_2 . To study the efficiency of the conversion of radiant into electrical energy, sensitive methods have been developed which involve: (a) the use of a selectively permeable membrane to separate the major part of the oxidizing electrolyte component Ox from the Ag-AgCl electrode A; (b) an increasingly careful control of the concentration of Ox present in contact with electrode A; and (c) the use of minimal starting amounts of both Ox and metallic Ag in our systems, together with the quantitative determination of the changes in these amounts resulting from irradiation.

When these changes were at first followed by measurements of the Ox concentration alone, possible effects of air oxidation introduced uncertainties into the results. However, the nearly complete elimination of metallic Ag from our freshly prepared electrode A (made possible by a pre-treatment of the surface of a Pt-electrode subsequently covered by an impervious AgCl layer) resulted in a markedly improved sensitivity, and enabled us to measure quantitatively the amount of photochemically formed Ag capable of yielding a useful electrical current I_u .

A theoretical model predicting that $I_u = K_1 / [k_2 + (\text{Ox})]$, where K_1 and K_2 are constants for a given system and a given constant illumination, and (Ox) is the concentration of Ox, appears to agree with our preliminary experimental data. The model assumes that I_u is limited in our experimental systems mainly by a parasitic corrosion reaction between Ox and Ag. For example the quantum yields corresponding to our maximum I_u were only about 2 to 5 percent, whereas the yields obtained photochemically with powdered AgCl were at least twenty times higher. It appears, however, that the upper limit for I_u has not yet been reached, and that I_u can probably be increased by a factor of ten or higher by appropriate changes in Ox and by means of suitable sensitizing and corrosion-inhibiting additives.

III. PROGRAM

It is proposed to conduct a program of research and development to obtain high efficiency, rechargeable batteries utilizing photogalvanic cell systems such as $\text{Ag/FeCl}_3\text{.aq./Pt}$.

This program will be conducted in two phases. The first phase will consist of both intensifying the study of the $\text{Ag-AgCl/FeCl}_3\text{/Pt}$ cell and evaluating other photogalvanic and nucleargalvanic cell systems; the feasibility of using one or more of these cell systems in a practical battery will be established. The second phase will be the development of the most promising reactions and the embodiment of these reactions in a reasonably packaged prototype. The experimental cells that are constructed will be tested under various conditions to determine their electrical characteristics. It is estimated that each of these phases will require twelve months to complete.

The investigations under this program include:

- A. The investigation of the $\text{Ag-Ag/FeCl}_3\text{/Pt}$ cell to improve the understanding of the factors affecting the efficiency of energy utilization in photogalvanic cells and to develop methods of maximizing this efficiency. The effects of photosensitizing and corrosion-inhibiting additives will be included in the investigation. The results will be extended to other silver halides or mixtures of halides.
- B. Concurrent with A, above, an investigation will be made of the reactions occurring in photogalvanic cell systems in general, and in nucleargalvanic cell systems, together with the evaluation of these systems for the efficient conversion of solar and nuclear energy.
- C. An investigation of the mechanisms and rates of electrode reactions as a function of incident radiation, and their spectral sensitivity.
- D. The investigation of electrode potentials and their dependence upon light intensity, wavelength, current drain and other operating conditions.
- E. The investigation of other photochemical, radiochemical, and supplementary electrochemical reactions to select the most suitable photogalvanic and nucleargalvanic electrodes. The electrodes selected will be used in the fabrication of experimental cells.

IV. FACILITIES

The optical equipment [redacted]
[redacted] includes a Farrand double-prism monochromator and a model 112 Perkin-Elmer spectrometer with associated automatic recording and wavelength drive mechanisms. One or both of these instruments will be utilized to obtain accurate measurements on the response of the batteries to light of various wavelengths. A standard light source has been ordered for the purpose of calibrating the monochromator according to absolute values of radiation intensities.

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A laboratory is available in which nuclear materials can be handled safely. Work in this laboratory is to be directed exclusively towards studying and developing electrolytic batteries of the type described above which can be reenergized by nuclear radiation. The scalers and radiation detectors necessary for the measurement of the nuclear radiation have already been purchased.

V. SCHEDULE OF DELIVERIES

[] will provide engineering services and technical reports in accordance with the following schedule:

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Description of Items	Due Date
I Program of photogalvanic and nucleargalvanic cell research as outlined in Section III.	Twenty-four months after date of award of contract.
II Monthly letters outlining the progress of work.	Monthly, beginning 15 days after the first month of work.
III Quarterly reports describing the problems, methods of approach and accomplishments of the report period in detail.	Quarterly, beginning 30 days after the end of the first quarter.
IV A final detailed report covering the entire program of work.	45 days after the end of the contract period.

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